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(54) **Carbon-cloth-based electrocatalytic gas diffusion electrodes of electrochemical cells and method of manufacture**

(57)   This invention pertains to gas diffusion electrodes and diffusers with new improved structures suitable for systems using ion conducting membranes as the electrolyte, and automated methods of manufacture that lend themselves to continuous mass production. Unexpected improvements in gas and vapor transport through the electrode are realized by incorporating a new dispersion process in the construction, reformulating the applied mix with solution additives, and creating a novel coating structure on a conductive web. Furthermore, combining these changes with a judicious choice in coating methodology allows one to produce these materials in a continuous, automated fashion.

FIGURE 1
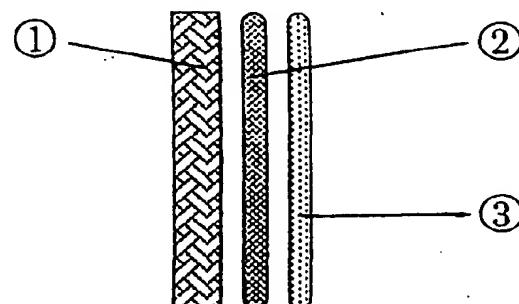
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Description

BACKGROUND

5   [0001]   A gas diffusion electrode (GDE) consumes or is depolarized by a gas feed while allowing direct electronic transfer between the solid and gas phase. Together with the electrolyte, the GDE provides a path for ionic transfer, which is just as critical. GDEs are typically constructed from a conductive support, such as a metal mesh, carbon cloth, or carbon paper. This support is often called a web. The web is coated with hydrophobic wet-proofing layers, and finally, a catalytic layer is applied most commonly to one face. While the catalytic layer can consist of very fine particles of a
10   precious metal mixed with a binder, many employ the methods similar to that in Petrow, et al., U.S. Patent No. 4,082,699. This patent teaches the use of finely divided carbon particles such as carbon black as the substrate for small (tens of angstroms) particles of the noble metal. Thus called a "supported" catalyst, this methodology has shown superior performance and utilization of the catalyst in electrochemical applications.
     [0002]   Often, GDEs are cited as key components in fuel cells. Here, the anode is typically depolarized with hydrogen
15   while the cathode is depolarized with oxygen or air. The resulting products are energy in the form of electricity, some heat, and water. Examples of acid or alkaline fuel cells are well known. Some have also realized that the energy-producing quality of a fuel cell can be adapted to industrial electrochemical processes and thus save energy and hence reduce operating costs. A typical chloralkali cell uses two solid electrodes to produce sodium hydroxide, hydrogen and chlorine. In this case, both the anode and cathode expend energy to evolve gas, chlorine and hydrogen respectively.
20   The typical chlor-alkali cathode can be replaced with an oxygen-depolarized cathode, as has been shown by Miles et al. in U.S. Patent No. 4,578,159 and others. A cell run in such a manner saves approximately one volt. Aqueous hydrochloric acid is an abundant chemical by-product. One can recover the high-value chlorine by oxidizing solutions of HCl, and thus recycle the chlorine as a feedstock to the chemical plant.
     [0003]   Electrolysis becomes extremely attractive when the standard hydrogen-evolving cathode is substituted with
25   an oxygen-consuming gas diffusion electrode due to the significant drop in energy consumption.
     [0004]   GDEs also may allow the creation of a commodity directly from a gaseous feedstock. For example, Foller, et al. (The Fifth International Forum on Electrolysis in the Chemical Industry, November 10-14, 1991, Fort Lauderdale, Fl., Sponsored by the Electrosynthesis Co., Inc.) describe the use of a GDE to create a 5 wt.% hydrogen peroxide in caustic. In this case, oxygen is the feedstock and a specific carbon black (without noble metals) is the catalyst.
30   The ability of the gas diffusion electrode to operate successfully in this and the preceding examples is acutely dependent on the structure of the gas diffusion electrode: for in all these cases, the electrode serves as a zone for liquid-gas-solid contact, as a current distributor, and most importantly, as a liquid barrier.
     [0005]   The advent of ion exchange membranes has greatly expanded the use of gas diffusion electrodes. The ion exchange membrane, which replaces the traditional liquid phase, is composed of a solid polymer electrolyte that trans-
35   fers ionic charge thanks to fixed ion exchange groups attached to the backbone chains. The most popular ion exchange membrane is sold by the DuPont Company, USA under the trademark Nafion®. It comprises a perfluorinated backbone with attached fixed ionic groups such as sulphonic or carboxylic radicals. Other Companies, such as Gore Associates, Asahi Chemical and Asahi Glass commercialize similar products. Non-perfluorinated ion exchange membranes are available through Raipore (Hauppauge, New York) and other distributors such as The Electrosynthesis Co., Inc. (Lan-
40   caster, New York). Anion exchange membranes typically employ a quaternary amine on a polymeric support and are commercially available as well.
     [0006]   When gas diffusion electrodes are used in conjunction with ion exchange membranes, such as in the case of the membrane hydrogen/air fuel cell, their internal structure must be designed to allow efficient three phase contact between the solid electrode itself, the gaseous reactant, and the solid polymer electrolyte. In addition to providing a
45   zone for three-phase contact, the gas diffusion electrode structure aids in making electrical contact to the catalyst, enhances transport of reactant gasses into the zone, and provides for facile transport of product away from the zone (e.g. water vapor).
     [0007]   In addition to gaseous hydrogen and gaseous air, others employ a mixed phase system such as the methanol/air(O_2) fuel cell. Here, liquid methanol is oxidized at the anode while oxygen is reduced at the cathode. Another utili-
50   zation for ion-conducting membranes and gas diffusion electrodes includes the electrochemical generation of pure gasses [for example see Fujita et al. in *Journal of Applied Electrochemistry*, vol. 16, page 935, (1986), electro-organic synthesis [for example see Fedkiw et al. in *Journal of the Electrochemical Society*, vol. 137, no. 5, page 1451 (1990)], or as transducers in gas sensors [for example see Mayo et al. in *Analytical Chimica Acta*, vol. 310, page 139, (1995)].
     [0008]   The membrane and electrode structure (MEA) may be constructed by forcing the electrode against the ion
55   conducting membrane. United States Patents No. 4,272,353; No. 3,134,697; and No. 4,364,813 all disclose mechanical methods of holding electrodes against the conducting membrane. However, the effectiveness of a mechanical method for intimately contacting the electrode to the polymer membrane electrolyte may be limited since the conducting membrane can frequently change dimensions with alterations in hydration and temperature. Swelling or shrinking can alter

the degree of mechanical contact.

[0009] Thus, an alternative method of contacting the electrodes with the polymer membrane electrolyte involves direct deposition of a thin electrode onto one or both sides of the conducting polymer substrate. Nagel et al. in U.S. Patent No. 4,326,930 disclose a method for electrochemically depositing platinum onto membranes. Others have employed chemical methods whereby a metal salt is reduced within the polymer membrane [for example see Fedkiw et al. in *Journal of the Electrochemical Society,* vol. 139, no. 1, page 15 (1192)].

[0010] In both the chemical and electrochemical methods, one essentially precipitates the metal onto the ion conducting membrane. This precipitation can be difficult to control due to the nature of the ion-conducting polymer membrane, the form of the metal salt, and the specific method employed to precipitate the metal. As the goal of a thin, porous, and uniform metal layer is often not met via precipitation, practitioners have turned to other deposition methods. For example, a method for coating the membrane with an ink composed of the supported catalyst and solvent is disclosed by Wilson and Gottesfeld in the Journal of the Electrochemical Society, volume 139, page L28, 1992; and a method of using a decal to deposit a thin layer of catalyst or supported catalyst onto the ion-conducting membrane is summarized by Wilson et al. in Electrochimica Acta, volume 40, page 355, 1995. An uncatalyzed gas diffusion structure is subsequently placed against each catalyst layer deposited or applied to the membrane.

[0011] In a further alternative the catalyst is coated onto an uncatalyzed gas diffusion structure and then bonded to the membrane via mechanical, and/or thermal means. The uncatalyzed gas diffusion structure is variously called a "diffuser", an electrode "backing", "gas diffusion media", a "gas diffusion layer", or an "uncatalyzed gas diffusion electrode" and can predominate MEA performance during operation at high current density. The term diffuser will be hereafter used to encompass all these synonyms. A diffuser is a material that: 1) provides electrical contact between the catalyst and the electrochemical cell current collector, 2) distributes and facilitates efficient transport of feed gas or gasses to the catalytic layer, and 3) becomes a conduit for rapid transport of product(s) from the catalytic layer.

[0012] There are a few commercial providers for diffusers. Gore Associates (Elkton, MD) offer Carbel™, a conductive, microporous polymer. E-TEK, Inc. (Natick, MA) offers uncatalyzed versions of the gas diffusion electrodes found in their catalog. Of these, the uncatalyzed ELAT™ is listed as the best material for MEA applications.

[0013] The typical construction of the ELAT™ diffuser is detailed in U.S. Patent No. 4,293,396 by Allen et al.. Here, a carbon cloth serves as the web. Carbon black is prepared for application to the carbon web by using techniques listed in U.S. Patent No. 4,166,143 whereby solutions of Vulcan XC-72 or Shawinigan acetylene black (SAB) are mixed with water, ultrasonically dispersed with a sonic horn. Since the carbons are high surface area substances, it is important to prepare a uniform and stable suspension. Carbon blacks do not "wet-out" without a significant input of energy or shear into the solution. The ultrasonic horn performs this function of wetting-out by way of high frequency electrical energy directed from a stainless steel horn immersed in the solution which generates pressure waves through the vessel. Although suitable for limited production runs or R&D sized samples, there are several limitations to ultrasound. First, since the energy is projected from a single source, i.e., the horn, the power is a function of the distance from the horn, and will diminish significantly as one moves away. Second, as the action of the carbon black on the horn leads to abrasion and accelerated corrosion, the projected power spectrum emanating from the horn changes in time. For these reasons, ultrasound may not be appropriate for production of large quantities of diffusers. The dispersions are then mixed with Teflon® particles and filtered. Teflon is a registered trademark of the DuPont Company, U.S.A. for polytetrafluoroethylene. Layers of SAB mix serve as the wetproofing layer on each side of the web. Finally, layers of Vulcan mix are coated onto one side of the assembly. After the final coat, the assembly may be sintered in air at a temperature sufficient to cause the Teflon to flow, typically 300-350°C. Although the importance of mix penetration into the web is discussed, the actual coating method is not disclosed. The reported products were of limited lot size, so may have been individually prepared. No information is relayed as to how this structure could be produced with economical means.

[0014] With the rise of membrane fuel cells, based on proton exchange membranes (PEM fuel cells) as suitable clean power sources, and the parallel increase in the use of MEAs in industrial and sensor applications, there is a strong need for a diffuser having a tailored and optimized structure. In addition, improvements are necessary in both the preparation of the dispersions as the current routine use of the sonic horn produces carbon black dispersions for coating that may be non-uniform and difficult to control for production of large batches of diffuser, and in the manufacturing methodology as the current procedure is limited in its applicability to continuously coating a web - a step believed to be crucial in producing an inexpensive product.

OBJECTS OF THE INVENTION

[0015] It is an object of this invention to provide improved gas diffusers with transport properties suitable for MEA type electrodes.

[0016] It is another object of the invention to provide diffusers with a catalytic layer directly applied thereto (hereinafter called gas diffusion electrodes).

[0017] It is a further object of this invention to introduce a dispersion methodology that provides an unexpected increase in performance from diffusers and gas diffusion electrodes fabricated from carbon blacks prepared by this technique.

[0018] It is a still further object of this invention to introduce for both diffusers and gas diffusion electrodes a method of manufacture that is compatible with continuous automation.

[0019] These and other objects and advantages of the invention will become obvious from the following detailed description.

THE INVENTION

[0020] The type A and type B diffusers of the invention, are schematically illustrated in Figs. 1a and 1b respectively and are compared with a prior art gas diffuser, Fig. 1c, which is commercialized under the trade mark ELAT™.

[0021] The prior art ELAT™ structure comprises an electrically conductive web (1), which is preferably made of carbon cloth or carbon paper or a metal mesh, highly hydrophobic layers (2) on both sides and more hydrophilic layers on one side (3).

[0022] All layers in Fig. 1 are obtained applying a mix of carbon black and binder particles, preferably particles of polytetrafluoroethylene, for examples Teflon® produced by DuPont, USA. The degree of hydrophobicity or hydrophilicity depends on the type of carbon black, which may be selected in the group comprising SAB, Vulcan XC-72, Black Pearls 2000 or Ketjen Black. Just as an example, it must be remembered that SAB is highly hydrophobic, while Vulcan XC-72 is more hydrophilic. The hydrophobicity and hydrophilicity may also be varied on the basis of the quantity of binder which is included in the various layers. In the most common case where the binder is polytetrafluoroethylene, which is highly hydrophobic, its quantity is normally comprised between 5 and 80% by weight, more preferably between 30 and 70% by weight, with higher quantities for more hydropbobic layers and lower quantities for more hydrophilic ones. In the schematic view of fig. 1, each layer represents a coat, however, the depicted number of coats should not be taken as a limitation of the invention. Actually, the number of coats is usually comprised between one and eight, as is shown in the examples.

[0023] As it should be clear from Fig. 1c, the prior art ELAT diffuser comprises two types of coatings characterized by different hydrophobicity, the most hydrophobic coating (2) being applied on both faces of the web.

[0024] Making reference to fig. 1a, it is clear that the diffuser of type "A" has a structure similar to that of the ELAT diffuser, as also this diffuser comprises two types of coatings having different hydrophobicity (2, 3) applied to one face of the web only. The most hydrophobic coating (2) is the one directly contacting the web.

[0025] The simplest of the diffuser structures of the invention is represented by type "B" which includes only one type of coating, applied on one face only. Fig. 1b illustrates the embodiment comprising he hydrophobic layer (2). However, it must be understood that also the hydrophilic layer (3) only can be applied.

[0026] The diffusers of fig. 1 are pressed or better bonded to MEA structures, that is membranes having surfaces coated with a thin film of catalyst.

[0027] The structures of fig. 1 represent also the corresponding gas diffusion electrodes when, in the case of prior art ELAT gas diffusers and type "A" gas diffusers of the invention, the hydrophilic coatings (3) and the only coating of type "B" (2 or 3) are obtained at least in part by using supported catalyst instead of plain carbon black. The gas diffusion electrodes obtained in this way are pressed or better bonded to membranes which have uncoated surfaces. Before obtaining this pressing or bonding, it is customary to apply onto the layer of the gas diffusion electrode containing the supported catalyst a final layer of a ionomer having ion-exchange characteristics similar to those of the polymer of the membranes. For example, 5-10% by weight solutions of Nafion may be used in a water-alcohol mixture, the so-called "liquid Nafion". The film, which comprises from 0.1 to 2 mgr/cm^2 of Nafion, is directed to aid in making contact with the membrane.

[0028] In comparing diffuser type "A" to the standard ELAT diffuser, one notes both a reduction in the number of coated layers, which translates to less total deposited solids, and the coating layers being placed on only one side of the carbon cloth web. The uncoated side of the web is now oriented toward the gas feedstream while the coated layers are placed against the MEA (i.e., the face of the membrane electrode assembly). As will be shown in the Examples, these reduced layers and single-sided coatings allow for a reduced number of fabrication steps, and a thinner, more open structure amenable to high gas flux rates.

[0029] For diffuser type "A", there are still two or more types of carbon black employed in the architecture of the structure. These are selected so as to create a gradient of hydrophobicity throughout the structure, as well as to provide a layer that can be more easily wetted at the catalyst interface. However, there are applications where a single kind of carbon black is appropriate, and diffuser type "B" in Figure 1 illustrates this alternative structure. For diffuser type "B", one or more coats of carbon black and binder are applied on one side of the web. This diffuser would be orientated as type "A", that is, the uncoated side is towards the feedgas plenum while the coated side is against the face of the MEA. Diffuser type "B" is easier to fabricate, and is the least expensive to manufacture.

[0030]   While much focus has been made on the structure and performance of gas diffusion electrodes, little contribution has been made in the nature and effect of carbon black preparation methods for gas diffusion electrodes. While the sonic horn is frequently cited, it is shown here that surprising enhancements in diffuser and gas diffusion electrode performance through other dispersion methods can be obtained. For example, one preferred method introduces a pressurized flowing stream of solvent and carbon black into a "Y" shaped chamber that divides the flow into two streams, which are recombined downstream using another "Y". The effect of splitting and recombining the stream introduces high shear and pressure differences on the solvent and carbon black, and effectively wets out the particles in a uniform and consistent manner. A commercial device is available through such companies as Microfluidics (Newton, MA). Other methodologies use rotor/stator methodology whereby one set of blades is fixed while the another set is spun at high rates around the fixed set. Such action creates high shear on the sample. Rotor/stator operations are often performed in batch mode. Another device is a mill where a spinning barrel with plates performs the function of delivering shear energy to the solution. Kady Company (Scarborough, ME) provides a range of these machines. These and similar devices are called "homogenizers" and perform the vital function of dispersing solids into solvent in a uniform and consistent manner. The following Example section describes such a preparation and reports results for diffusers and gas diffusion electrodes unanticipated by simple homogenization of the carbon black solution.

[0031]   While the placement and number of carbon black layers can control structure, and the method used to disperse the carbon black also determines performance, the technique employed to coat a web with mix determines the final structure as well. The previously cited ELAT patents describe a successful coating on the carbon cloth web which results from physically penetrating into the woven structure to encase the fiber bundles with mix. A coating methodology most appropriate for this function is slot-die, knife-over-blade, or spraying followed by a knife operation. Slot-die coating is the preferred method as the slot acts as a control mechanism that meters out a fixed amount of mix. The weight of solids placed on the web is determined by the line speed, pump rate through the slot die, and mix composition (% solids). Furthermore, since the slot-die acts through creating a constant mass of mix between the slot-die head and the moving web, this coating action serves to both give some penetration into the cloth and compensate for surface roughness inherent in the cloth.

[0032]   While slot-die has been used to coat various solid and porous substrates, using the slot-die to create gas diffusion electrodes and diffusers is a novel application. Typical widths of a slot-die range from 5-250 mm, but larger dies can be constructed. The gap of the slot die can be controlled via shims, a typical range being between 4 and 100 mils, and more preferably 15-30 mils. Both the coating of the mix and the size of the drying section of the coating machine determine the line speed, as the freshly coated web is next run into a heated chamber. Typical line speeds range from 0.1 to 5m/min. Multiple coats can be applied by a series of slot-die stations, or re-running a freshly-coated web through the machine. Other attachments to a manufacturing line would include a continuous sintering oven and a slitting machine to cut the final product into the desired dimensions.

[0033]   For mixes consisting of carbon black (or supported catalyst) and polytetrafluoroethylene, a Gravure style coating method can be employed as well. Gravure coating employs a spinning rod that is dipped in mix at the lower half and then contacted with the moving web at the other upper segment. Typically, the gravure-coating head spins in a direction opposite the direction of the moving web, allowing some penetration of the mix into the web. The quantity of the mix applied to the web per pass is controlled by the mix rheology, line speed, gravure rotation speed and gravure imprint pattern, and the area of the web contacting the head. Gravure coating works best with low viscosity mixes.

[0034]   The selection of a coating method such as slot-die, gravure, knife-over-plate, or spraying is dependent on the fluid dynamics of the mix, mix stability during the coating process, and the electrode and/or diffuser structure desired on the web. One is not limited to one coating method. Typically, more than one coating station can be applied to the moving web to build-up a multi-layer structure if so desired, whereupon the selection of coating station is dependent on the requirements of the mix.

[0035]   In some cases, the composition of the dispersed carbon black mix is modified by adding additives such as iso-propyl alcohol (from 0.1 to 100%, more commonly between 5 to 30%, and preferably 25%), Fluorinert FC 75 or similar, Neoflon AD-2CR, polyvinyl alcohol, Polyox®, or similar stabilizers.

[0036]   In some operations it is preferable to avoid iso-propyl alcohol, for example due to the constraints and costs of handling organic vapors, and a water-based mix is employed. For this type of mix, one or more of the following stabilizers and thickeners can be employed: Fluorinert FC 75 or similar, Neoflon AD-2CR, polyvinyl alcohol, ethylene glycol, polyethylene glycol alkyl ether, Polyox®, Triton® X100, Tween®, Joncryl 61J, Rhoplex AC-61, Acrysol GS (acrylic polymer solutions; and naphtalene formaldehyde condensate sulfonates.

[0037]   When using supported catalyst, the catalyst may be any of those conventionally used such as platinum or a rhodium-rhodium oxide catalyst described by E. De Castro at the Electrochemical Society Meeting held in San Diego on May 3-8, 1998. The specific coating method and stabilizer is dependent on the structure of diffuser desired.

[0038]   In the following examples, there are described several preferred embodiments to illustrate the invention. However, it should be understood that the invention is not intended to be limited to the specific embodiments.

PREPARATION EXAMPLE 1

[0039] A standard ELAT is constructed for comparison with diffuser or gas diffusion electrode structures of type "A" or "B". A web consisting of carbon cloth with a warp-to-fill ratio of unity, with approximately 25 to 50 yarns per inch, and a carbon content of 97-99% was selected from an available thickness of 5-50 mils, preferably around 10 mils. The same carbon cloth was used for any diffuser or gas diffusion electrode of the following Examples. An appropriate weight of SAB or Vulcan XC-72 was dispersed with an ultrasonic horn. A dispersion of Teflon particles, was added to the mix to form a 50% wt (solids) component. To the web, a first mixture of dispersed SAB was hand coated onto each side by using a spatula, until coverage of approximately 3.5-7 mg/cm² was obtained. This layer was considered the hydro-phobic, also called wet-proofing, layer. The electrode was air dried at room temperature in between each coat. To this dried assembly, a second but similar mix of supported platinum catalyst on Vulcan XC-72 and Teflon was coated on one side. Between one and eight coats were provided to achieve the desired metal loading, typically 0.2 to 0.5 mg catalyst/cm². After the final application, the coated web was heated to 340°C for about 20 minutes. As described, a gas diffusion electrode was obtained. To make a diffuser, similar steps are performed except uncatalyzed Vulcan XC-72 is employed.

PREPARATION EXAMPLE 2

[0040] To construct a gas diffusion electrode or diffuser of type "A" structure of the invention, an identical procedure as outlined for Example 1 was followed, except the SAB/Teflon wetproofing layer was applied by hand to one side of the web at approximately half the total carbon black loading, i.e. 1.5-3 mg/cm². The catalyzed Vulcan XC-72 coat and final treatment followed that as detailed above. To make a diffuser, similar steps were performed except uncatalyzed Vulcan XC-72 with a loading range of 0.5-1.5 mg/cm² carbon black was employed.

PREPARATION EXAMPLE 3

[0041] To construct a gas diffusion electrode or diffuser of type "B" structure of the invention, an identical procedure as outlined for Example 2 was followed. However, only the catalyzed SAB/Teflon wetproofing layer or catalyzed Vulcan XC-72 was applied to one side of the web at total loading of approximately 0.5-5 mg/cm². Similar drying and heating steps as Example 1 followed. A diffuser was constructed in an identical manner except either SAB or Vulcan XC-72 without catalyst was employed.

PREPARATION EXAMPLE 4

[0042] A type "B" gas diffusion electrode similar to that of Example 3 was constructed through an automated coater. For this example, a knife-over-plate coater was used and the coater employed a 255 mm perpendicular stainless steel blade with a 45°C beveled edge. The blade was positioned over the cloth with a fixed gap of approximately 10 mils. The line speed was 2 meters/min., and mix, prepared as in Example 3, was fed at continuous rate to a reservoir in front of the blade. Samples thus prepared were subjected to the same heating and drying steps of Example 1.

PREPARATION EXAMPLE 5

[0043] Homogenized mixes of carbon black were created through the use of Microfluidic's microfluidizer. A suspension of water and appropriate weights of either SAB or Vulcan XC-72 was fed to the machine, which was pneumatically operated. A single chamber configuration was employed using the 100 micron chamber, although other chamber sizes could be used as well. After a single pass through the homogenizer, Teflon was added to the mix in the same proportion as established in Example 1. The mix was filtered, and coated onto a carbon web as detailed in Example 1 or Example 2.

PREPARATION EXAMPLE 6

[0044] To prepare a diffuser similar to Type "A" with the slot die coating methodology, a mix similar to that described in Example 5 is prepared, except prior to filtering a finite amount of Triton X100 is added to the carbon black solutions to make up approximately 1% weight Triton X to weight of carbon black. A typical range for this additive is 0-5% based on weight of carbon black. Furthermore, some dissolved Polyox is added to the solution in the amount of 10% weight based on carbon black. The typical range for this additive is 0-20% based on the weight of carbon black. Excess solution is then removed by filtering.

[0045] A mix of Shawingan Acetylene Black (SAB) or Vulcan XC-72 as prepared above is placed in a pressurized vessel that is connected to the slot die. A pressure of 10-15 psi is applied to the vessel to deliver mix to the slot-die

head at an appropriate rate. The 250 mm long slot die is oriented to ride on the carbon cloth web, a gap of 18 mils is set for the slot die. For both the SAB and Vulcan mixes, the web passes the coating head at 2 m/min. Multiple coats of SAB and Vulcan are applied to the web until an appropriate weight of carbon is distributed. The coated cloth is dried prior to each additional coat. The final assembly is sintered at 340°C for 20 minutes prior to testing.

PREPARATION EXAMPLE 7

[0046] To prepare a catalyzed gas diffusion electrode similar to Type "A" with the gravure coating methodology, a mix similar to that described in Example 5 is prepared, except now less water is removed and a less viscous consistency is attained. Also, the Vulcan XC-72 is catalyzed with a 30% by weight of platinum. A carbon cloth is rolled past a 12.7 mm diameter, 250 mm long gravure head that is rotating at 100 rpm. This gravure head has 5.3 cell/cm^2 pattern across the surface to aid in pick-up and distribution of the mix. The web is first coated with SAB at the rate of 2 m/min. Several coats are applied with air drying in-between coats. Next several layers of 30% Pt on Vulcan XC-72 are applied at 1 m/min, with drying in-between coats. The final assembly is sintered at 340°C for 20 minutes prior to testing.

EXAMPLE 8

[0047] In order to illustrate various aspects of the new diffuser structures of the invention, a series of diffusers is prepared and compared to the commercially available ELAT™ diffuser. Several type "A" diffusers of varying thicknesses are prepared according to the methods described in Example 2, except the total weight of solids is increased or decreased to adjust the final assembly's thickness. A type "B" diffuser of SAB was prepared according to the methods described in Example 3. For both these Type "A" and "B" diffusers, the methodology of dispersion of Example 5 is employed. Table 1 summarizes the key differences among the various coatings. The thickness of each diffuser is taken with nine measurements across the entire (100 cm^2 sample. A representative thickness of each type of diffuser is the total average of these nine measurements and number of samples.

TABLE 1

Diffuser type	Description	Thickness +/- mils	No. samples
B	Uniform thin hydrophobic microporous layer	17.0+/-0.6	4
A	Composite of very thin hydrophobic and hydrophilic microporous layers	15.6+/4.2	4
A	Standard composite of thin hydrophobic and hydrophilic microporous layers	16.2+/-0.7	5
A	Thick composite of hydrophobic and hydrophilic microporous layers	18.8+/-1.0	4
Standard ELAT™	Coatings on both sides of web	19.4+/-0.6	6

[0048] For porous and/or fibrous gas filtration media, resistance to flow is often used as a characteristic measure for quality control and performance. This measurement is standardized and so widely performed that a commercially produced instrument is employed, called a "Gurley" device. The Gurley number is the time it takes to move a fixed pressure through a fixed area of sample, and thus the Gurley number indicates the resistance to gas flow. As the diffuser permeability is an important parameter for optimized operation, the Gurley number is a good method for quantitative characterization.

[0049] To determine the "Gurley" number of the various diffusers, an apparatus for measuring resistance to flow was constructed employing two water-filled "U" barometric tubes, one 80 and the other 40 cm long, a nitrogen flow meter (0-20 LPM), and a back-pressure valve. Samples of electrode backing (10 x 10 cm) are cut and fitted into a manifold with gaskets (5 x 5 cm exposed area), such that the uncoated side of the backing is oriented towards the nitrogen inlet. Prior to fitting a sample in the manifold, the system's inherent resistance to gas flow is evaluated by measuring back-pressure in the barometric U-tubes, over a range of flow rates. This system "resistance" is used as a correction in subsequent diffuser measurements.

[0050] In order to first establish an appropriate evaluation range, five samples of standard Type "A" diffusers were subjected to a series of output flow rates. These output rates are fixed by progressively increasing the input flow through the output back-pressure valve and/or input flow rate, and noting the output flow, and input and output U-tube pressure. The output flow was varied from 1 to 7 LPM. Pressure differentials, corrected for the system resistance, are calculated and the output flow rate in LPM is divided by the differential pressure in units of cm of H_2O, which is then normalized

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to the exposed backing area of 25 cm². The resulting value is the characteristic constant for resistance to flow and is similar to the Gurley number. A plot of output flow versus the calculated resistance to flow shows that non-uniform flow is realized at the low and high flow rates, and an output range of 2-4 LPM is best for these measurements on diffuser materials. Based on this result, an output flow of 3.0 LPM was selected for subsequent comparative measurements.

[0051] An additional effect of the diffusers when used in PEM fuel cells is related to its role in helping to maintain water balance. Water balance in the fuel cell entails a delicate balance of hydrophobic and hydrophilic character within the coating. This balance depends critically on operating parameters such as current density of operation (which determines how much water is generated), humidification conditions and the flow rate of gases into the cell. Thus, depending on how the fuel cell is run with regards to current density, hydration, type of ion exchange membrane, and flow characteristics to the diffuser, the hydrophilicity of the coating is also crucial as well as the structure of the diffuser. Thus, to illustrate how different diffuser structures effect transport under a constant set of operating conditions, these same samples were evaluated in a single cell of a PEM fuel cell testing apparatus.

TEST EXAMPLE

[0052] Samples of ELAT or type "A" gas diffusion electrode were subjected to small scale tests in an apparatus designed to remove system influences from the experiment. That is, typical operation of a fuel cell or electrochemical process may be dependent on cell design, assembly, and system control parameters. This test used an electrolyte solution and catalyzed electrode to eliminate contact variance between the typical diffuser and MEA. Thus, the catalyst in this system was "wetted" and the results reflect electrode structural differences when the same catalyst and catalyst loading were employed.

[0053] A gas diffusion electrode holder (I cm dia.) was constructed whereby the catalyzed face was positioned in a solution containing 0.5M H_2SO_4 while the backside was subjected to an open gas plenum of approximately 20 cc. A potentiostat and three electrode set-up were employed to precisely control the applied potential to the test sample. A sheet (2.5 x 2.5 cm) of platinum served as the counter electrode. Standard ELAT samples containing 30 % Pt/C, 1 mg/cm² were prepared using the method of Example 1. Type "A" electrodes were fabricated according to the steps of Example 2, whereupon the catalyst and loading was the same as the ELAT. Each electrode was sprayed with Nafion resulting in a coverage of 0.5 mg/cm². After mounting in the holder, samples were immersed in the acid solution, which had been heated to approximately 55°C. The electrodes were first fed with oxygen at a stoichiometric excess (greater than 10 fold) under a very slight pressure ~2 mm H_2O) for conditioning as negatives potentials were applied vs. saturated calomel electrode (SCE) to reduce oxygen. After the exposure to oxygen, the cell was disconnected, flushed with nitrogen, and hydrogen was fed to the electrode under the same slight pressure and stoichiometric excess. Positive potentials were applied and the current was recorded. No accommodation for IR was made in the measurements, although 0.5-1. ohm had been measured through the electrode holder. Multiple samples from each ELAT or type "A" gas diffusion electrode were tested and averaged and the reported error bars were one standard deviation.

[0054] Figure 2 is a plot of these tests. The applied potential is listed on the abscissa, while the resulting current due to hydrogen oxidation is displayed on the ordinate axis. Since the catalyst and wetting characteristics were identical for these structures, one concludes that the increase in current for type "A" over the ELAT gas diffusion electrode was due to the improved structure of the type "A" electrode.

[0055] The surprising effect of homogenized carbon is shown in Figures 3 and 4. In this test, standard ELAT diffusers were prepared as outlined in Example 1 but now used homogenized SAB and Vulcan XC-72 as described in Example 5. The three different gas diffusion electrodes (standard ELAT, ELAT with homogenized wet proofing layer, and ELAT with both SAB and Vulcan layers homogenized) were tested using the same testing procedure as detailed above, except both the oxygen and hydrogen curves were recorded. Figure 3 is the oxygen reduction curve. Although there was some scatter in the data, attributed to uncompensated IR, it can be seen that as the layers were progressively homogenized, greater reductive (or negative) currents were generated for a fixed potential. A significant and unexpected improvement in ELAT performance was realized through homogenization of the carbon blacks. Figure 4 is a similar plot except the electrode was used as an anode in ambient hydrogen and a significant and unexpected improvement was shown.

[0056] The same electrodes were next assembled in a fuel cell system to confirm the improvement. For this test, a standard fuel cell test station (Fuel cell Technologies, Inc. NM) was used to control and humidify feed gasses, provide an electronic load, and record data from a cell 16 cm². For these tests, electrodes were mechanically compressed against a Nafion 115 membrane to form the MEA. An ELAT with homogenized SAB and Vulcan XC-72 layers was used as a cathode, and the test was performed in air and oxygen. Figure 5 shows the average results of five replicate standard ELAT diffusers compared to a typical homogenized carbon black ELAT when using air as the oxidant. For these plots, the fixed cell voltage is listed on the ordinate, while the recorded current is on the abscissa. Figure 6 is similar to Figure 5 except pure oxygen was the oxidant. In both Figure 5 and Figure 6, an improvement was seen for these electrodes in an actual system. It is surprising that a simple processing step, i.e. homogenization, produces such

an increase in current for a fixed voltage (greater power).

[0057] The next example combined the improvements of carbon black homogenization with the new structures. A type "A" diffuser was constructed according to the homogenization procedure of Example 5. Since this was a diffuser, it was assembled as part of a MEA whereby the catalyst layer has been deposited directly on the ion conducting membrane. In this test, comparison was made with a standard ELAT diffuser and the type "A" structure in a fuel cell set up incorporating a cell 50 cm². The cell was operated with hydrogen and air, and the load was systematically varied. Figure 7 shows data that revealed an improvement unanticipated by either structural or homogenization changes alone. The trace labeled "old" is the standard ELAT diffuser and the trace labeled "new" is the new diffuser structure with homogenized carbons. At the extreme loads, there was a test of a diffuser's ability to transport oxygen and water vapor, and it shows a remarkable 100% improvement in current density for a cell voltage of around 0.4 volts. This example clearly shows a remarkable synergistic effect between the carbon dispersion and new diffuser structures.

[0058] Although the above examples have used fuel cell tests, diffusers and MEAs can be used in industrial electrochemical processes as well. A type "B" hand-made gas diffusion electrode composed of platinum catalyzed Vulcan XC-72 pressed against a Nafion 430 membrane was constructed and this same style of electrode was then manufactured through the knife-on-plate method described in Example 4. The performances of these cathodes operating as oxygen consuming electrodes in a concentrated HCl solution were compared. Figure 8 summarizes the current potential curves derived from 6.25 cm² samples of type "B" assemblies. As shown here, the automated coating process did not introduce any significant changes in the structure of the electrode, and no difference in current was obtained.

[0059] A type "B" gas diffusion electrode composed by hand as illustrated in Example 2 is compared to a gravure method machine-coated Type "B" gas diffusion electrode as illustrated in Example 7, whereby the platinum content is within 10% of each other. The two electrodes are tested whereby 16 cm² samples of each are used as anodes and cathodes in a hydrogen-air PEM fuel cell at 70°C. Figure 9 summarizes the current potential curves derived from these samples. As shown here, the automated coating process did not introduce any significant changes in the structure of the electrode, and no difference in current was obtained.

[0060] The series of diffusers of Table 1 are used to illustrate the range of gas permeation rates made available by the structures of the invention by using the modified Gurley apparatus. A summary of resistance to flow measurements for the three types of electrode backing are shown as a bar chart in Figure 10. For the Type "A", three different thicknesses of carbon black were tested. One would anticipate that the resistance to flow should increase as the diffuser thickness increases. This trend is followed by the data. The standard double sided ELAT and thick Type "A" diffuser show a greater resistance to flow than the standard Type "A". It is interesting to note that the thin Type "A" diffuser shows the greatest relative standard deviation across the average of measurements, indicating that the microporous coating of carbon black may have random pin-holes and thus show lower resistance to flow than the standard Type "A". These data demonstrate that one can adjust the porosity and tortuosity in the diffuser structure, and that a suitable range of resistance to flow constants is over the range of 0.06 to 0.005 LPM/cm H₂O/cm², and more preferably from 0.05 to 0.008 LPM/cm H₂O/cm².

[0061] While porosity and tortuosity (as measured on a macroscopic scale by the Gurley measurements) do contribute to the performance (as will be shown here), other factors such as catalyst layer permeability and ionic conductivity, hydrophobicity and water transport through the coating may contribute more significantly to demonstrate these effects, the series of Table 1 was subjected to evaluation in a PEM fuel cell test apparatus.

[0062] A collection of polarization curves obtained with 100% oxygen and 13.5% O₂ in N₂ is shown in Figure 11. The results indicate that Type "A" thick and the standard ELAT diffusers exhibit limiting current behaviour at ca. 20% lower current densities than for the other cases. This suggests that the thicker coatings, with their lower gas permeation rates, exhibit more sensitivity to the particularly dilute portions of the cathode flow streams.

[0063] Although the uniformly hydrophobic Type "B" exhibits slightly lower performance relative to the thin and standard Type "A"s at the lower current densities, this diffuser has similar performance at high current density. Thus, there is some merit in creating a diffuser of completely uniform hydrophobicity. These results here indicate that a wide variety of structures are suitable for PEM fuel cells, and that the structure of the diffuser (or gas diffusion electrode) has to be matched to the specific operating conditions as well as cell design. All of these structures show an improvement over the standard ELAT design under dilute cathode feeds.

[0064] These examples demonstrate that new and unexpected advances in performance are obtained when combining homogenization in the preparation steps with new gas diffusion electrode structures. These are fabricated into MEAs by either assembling a diffuser with a catalyst-coated membrane, or by incorporating a gas diffusion electrode with the membrane. The step of homogenization can be used to prepare mixes for automated coating, and the new structures are capable of being produced in an automated fashion.

Legenda of the drawings

[0065] FIGURE 1 is a schematic of new diffuser and gas diffusion electrode structures where each layer of carbon

black represents a coat, although the depicted number of coats does not limit these embodiments.

[0066] FIGURE 2 is a three-electrode testing of standard ELAT gas diffusion electrode versus type "A" electrode and both electrodes were composed of 30 % Pt/C, 1 mg/cm^2 loading. Electrodes are constructed according to Example 1 and Example 2 specifications and tested in hydrogen at ambient pressure.

[0067] FIGURE 3 is a three-electrode testing of homogenized carbon in standard ELAT gas diffusion electrode. All electrodes were composed of 30 % Pt/C, 1 mg/cm^2 loading. Electrodes were constructed according to Example 5, whereupon either the wet proofing SAB or both the SAB and Vulcan layers were homogenized. Tested in oxygen at ambient pressure.

[0068] FIGURE 4 is a three-electrode testing of homogenized carbon in standard ELAT gas diffusion electrode. All electrodes were composed of 30 % Pt/C, 1 mg/cm^2 loading and constructed according to Example 5, whereupon either the wet proofing SAB or both the SAB and Vulcan layers were homogenized. Tested in hydrogen at ambient pressure.

[0069] FIGURE 5 is a fuel cell testing of standard ELAT gas diffusion electrode compared to standard ELAT constructed according to Example 5, whereupon both the SAB and Vulcan layers were homogenized. All electrodes were composed of 30 % Pt/C, 1 mg/cm^2 loading and MEA were assembled using a Nafion 115 membrane. The system was operated with hydrated gasses at 70°C, and hydrogen at 3.5 Bar (absolute) and air at 4.0 Bar (absolute). A two-fold stoichiometric excess of oxidant was fed based on the highest current density.

[0070] FIGURE 6 is a fuel cell testing of standard ELAT gas diffusion electrode compared to standard ELAT constructed according to Example 5, whereupon both the SAB and Vulcan layers were homogenized. All electrodes were composed of 30 % Pt/C, 1 mg/cm^2 loading and MEA was assembled using a Nafion 115 membrane. The system was operated with hydrated gasses at 70°C, and hydrogen at 3.5 Bar (absolute) and oxygen at 4.0 Bar (absolute). A two fold stoichiometric excess of oxidant was fed based on the highest current density.

[0071] FIGURE 7 is a fuel cell testing of standard ELAT diffuser (labeled "Old") compared to type "A" diffuser constructed according to Example 5 (labeled "New"), whereupon both the SAB and Vulcan layers were homogenized. An identical MEA was employed for each test and the system was run at two fold stoichiometric excess of air based on the 1 A/cm^2 while the hydrogen was continuously varied at two times stoichiometry based on the load requirements.

[0072] FIGURE 8 is a comparison of type "B" electrodes made by hand and by knife-over-blade automated coating. Both electrodes were composed of 30 % Pt/C, 1 mg/cm^2 and assembled with a Nafion 430 membrane to form the MEA. Oxygen was at a five fold stoichiometric excess with the highest recorded current, and a back pressure of upwards to 50 cm. H$_2$O was employed while a solution of 184 g/l HCl was circulated and kept at 55°C.

[0073] FIGURE 9 is a comparison of Type "A" electrodes made by hand and by gravure machine coating. Both electrodes were composed of 30% Pt/C: the hand made electrode at 1 mg/cm^2, and assembled with a Nafion 115 membrane to make a MEA The cell was operated at 70°C with hydrated gasses, and hydrogen at 3.5 Bar (Absolute) and air at 4.0 Bar (Absolute). A two-fold stoichiometric excess of air based on the highest current density was employed.

[0074] FIGURE 10 is a bar chart comparing the resistance to flow for a series of Type "A", a type "B", and a standard E-TEK ELAT described in Table 1. The average thickness for the group of samples is listed as well as one standard deviation of error in the bar graph.

[0075] FIGURE 11 is a comparison of current vs. potential for MEAs employing the various diffuser structures cited in Figure 10. Test conditions: 50 cm^2 cell, Pt loading 0.15-0.2 mg/cm^2 for anode and cathode whereby metal is deposited directly on a Nafion membrane.

[0076] The cell was operated at 80°C while the anode and cathode back pressure = 30 psig; 1.5 stoichiometric anode and cathode flow rate. Neat oxygen and 13.5 % oxygen are employed as the oxidants. Hydrogen is the reductant.

Claims

1. A gas diffuser comprising an electrically conductive web (1) and a layer (2, 3) containing carbon black particles and binder particles, **characterized in that** said layer is present on one surface only of the web and is obtained by coating said only surface of the web with a high-shear homogenized mixture of carbon black particles, binder particles and solvent.

2. The gas diffuser of claim 1 **characterized in that** said conductive web (1) is a carbon cloth, carbon paper or a metal mesh.

3. The gas diffuser of claim 1 **characterized in that** said high-shear homogeneized mixture is obtained by means of microfluidizers, rotor/stator equipment provided with blades, spinning barrel equipment provided with plates.

4. The gas diffuser of claim 1 **characterized in that** said binder of the mixture of carbon black particles, binder particles and solvent is hydrophobic.

5. The gas diffuser of claim 4 **characterized in that** said hydrophobic binder is polytetrafluoroethylene.

6. The gas diffuser of claim 5 **characterized in that** the polytretrafluoroethylene amounts to 50% by weight of the total solids contained in said mixture.

7. The gas diffuser of claim 1 **characterized in that** said mixture of carbon black particles, binder particles and solvent further comprises stabilizers chosen from the group of iso-propyl alcohol, Fluorinert FC 75, Neoflon AD-2CR, polyvinyl alcohol, ethylene glycol, polyethylene glycol alkyl ether, Polyox®, Triton® X100, Tween®, Joncryl 61J, Rhoplex AC-61, Acrysol GS (acrylic polymer solutions), and naphtalene formaldehyde condensate sulfonates.

8. The gas diffuser of claim 1 **characterized in that** said layer (2, 3) penetrates inside the electroconductive web (1).

9. The gas diffuser of claim 1 **characterized in that** said layer (2, 3) comprises one type only of carbon black particles.

10. The gas diffuser of claim 1 **characterized in that** said layer (2, 3) comprises two types of carbon black particles with different hydrophobicity, so as to create a gradient of hydrophobicity throughout the layer.

11. The gas diffuser of claim 1 **characterized in that** said layer (2, 3) comprises decreasing amounts of said hydrophobic binder from the web side to the external side to create a gradient of hydrophobicity.

12. The gas diffuser of claim 1 **characterized in that** its resistance to gas flow is comprised between 0.005 and 0.06 liters per minute/cm of water column/cm^2, and more preferably between 0.008 and 0.05 liters per minute/cm of water column/cm^2.

13. The gas diffuser of claim 1 **characterized in that** said layer (2, 3) is produced by means of one of slot-die, knife-over-blade, spraying followed by knife operation, gravure machine.

14. The gas diffuser of claim 1 **characterized in that** said layer (2, 3) comprises carbon black particles supporting fine particles of catalyst at least on its external surface.

15. The gas diffuser of claim 14 **characterized in that** said catalyst is chosen from the platinum group metals and their oxides.

16. The gas diffuser of claim 15 **characterized in that** said catalyst is platinum, rhodium or rhodium oxide.

17. A method of manufacturing a gas diffuser or gas diffusion electrode comprising :

   a) preparing a dispersion mixture of carbon black particles or catalyzed carbon black particles by using a high-shear homogeneizing equipment, such as microfluidizers, rotor/stator equipment provided with blades, spinning barrel equipment provided with plates;
   b) adding a binder to the resulting mixture;
   c) adding at least one dispersion-stabilizing substance to the mixture;
   d) coating an electrically conductive web on one side only with the mixture by using at least one gravure, slot-die, knife-over-blade spraying followed by knife, coating head;
   e) drying the coated wed and then
   f) sintering the coated web at 300-400°C.

18. The method of manufacturing of claim 17 **characterized in that** the stabilizing substance is selected from the group consisting of iso-propyl alcohol, Fluorinert FC 75, Neoflon AD-2CR, polyvinyl alcohol, ethylene glycol, polyethylene glycol alkyl ether, Polyox®, Triton® X100, Tween®, Joncryl 61J, Rhoplex AC-61, Acrysol GS (acrylic polymer solutions), and naphtalene formaldehyde condensate sulfonates.

19. The use of the gas diffuser of claims 1-13 **characterized in that** said gas diffuser is intimately contacted by one surface of an ion exchange membrane provided with a layer of catalyst, in an electrochemical cell.

20. The use of the gas diffuser of claims 1-13 **characterized in that** said a pair of gas diffuser is intimately contacted by an ion exchange membrane having both surfaces provided with a layer of catalyst, in an electrochemical cell.

21. The use of the gas diffuser of claims 14-16 **characterized in that** said gas diffuser is intimately contacted by one surface of an ion exchange membrane provided with a layer of catalyst, in an electrochemical cell.

22. The use of the gas diffuser of claims 14-16 **charact rized in that** said a pair of gas diffuser is intimately contacted by an ion exchange membrane having both surfaces provided with a layer of catalyst, in an electrochemical cell.

23. The use of claims 20 and 22 **characterized in that** said electrochemical cell is a fuel cell.

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FIGURE 1
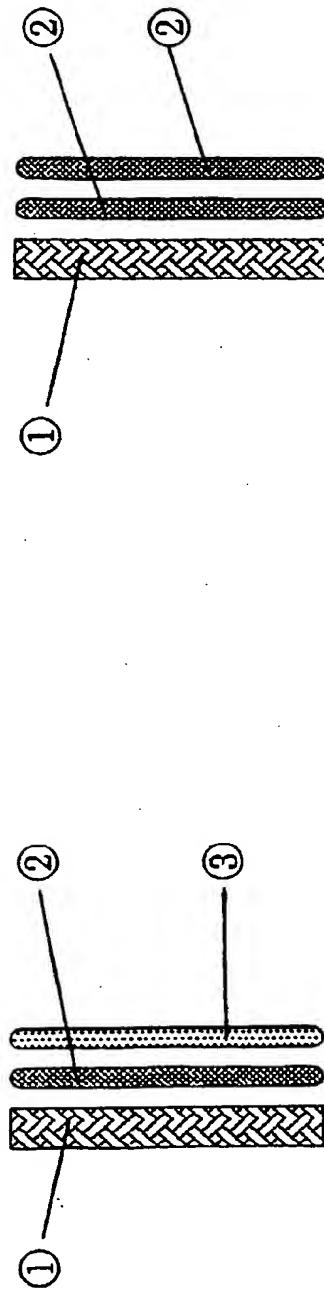
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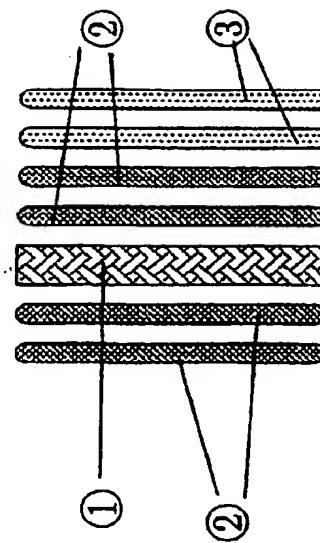
1b

1c
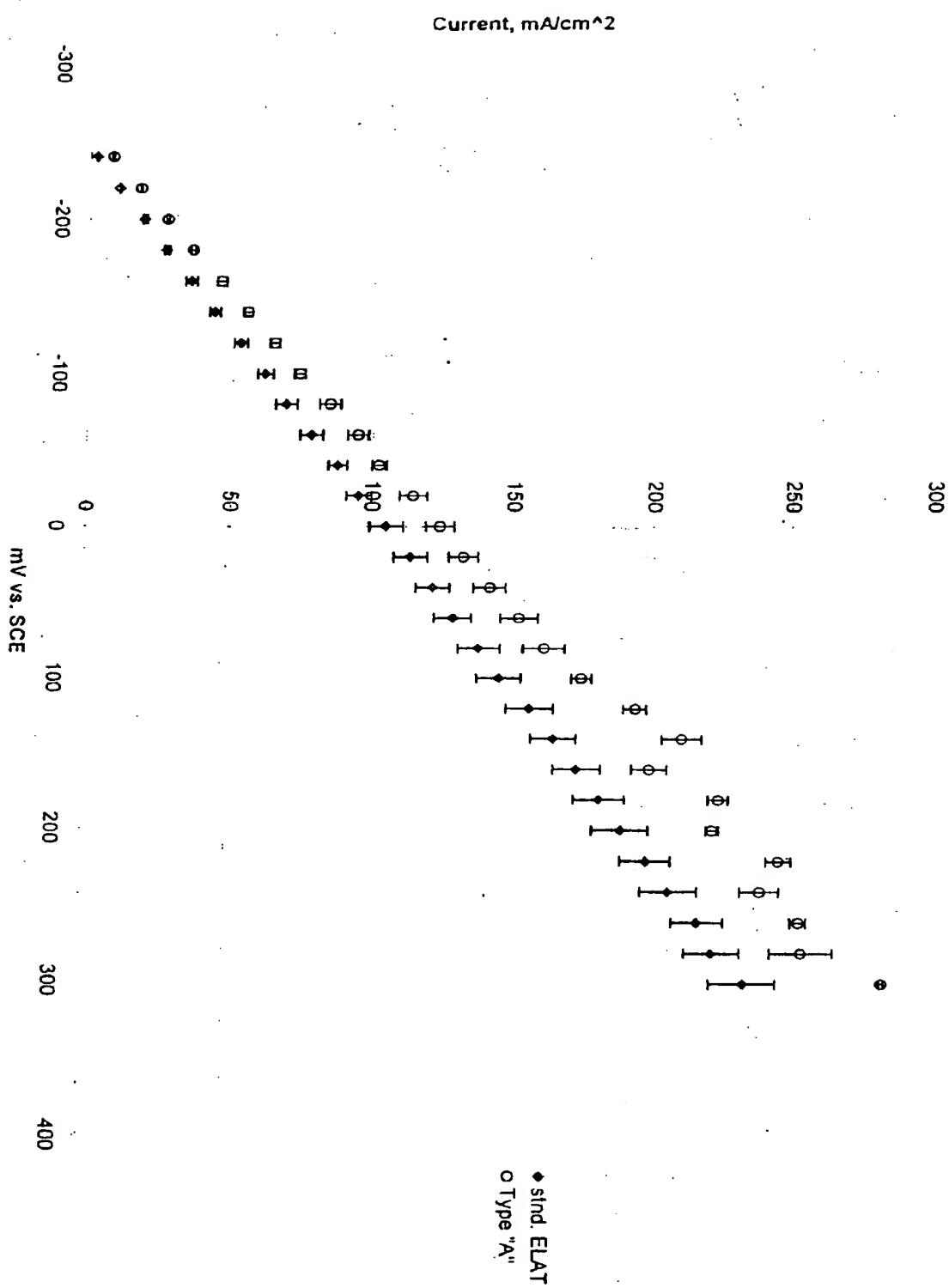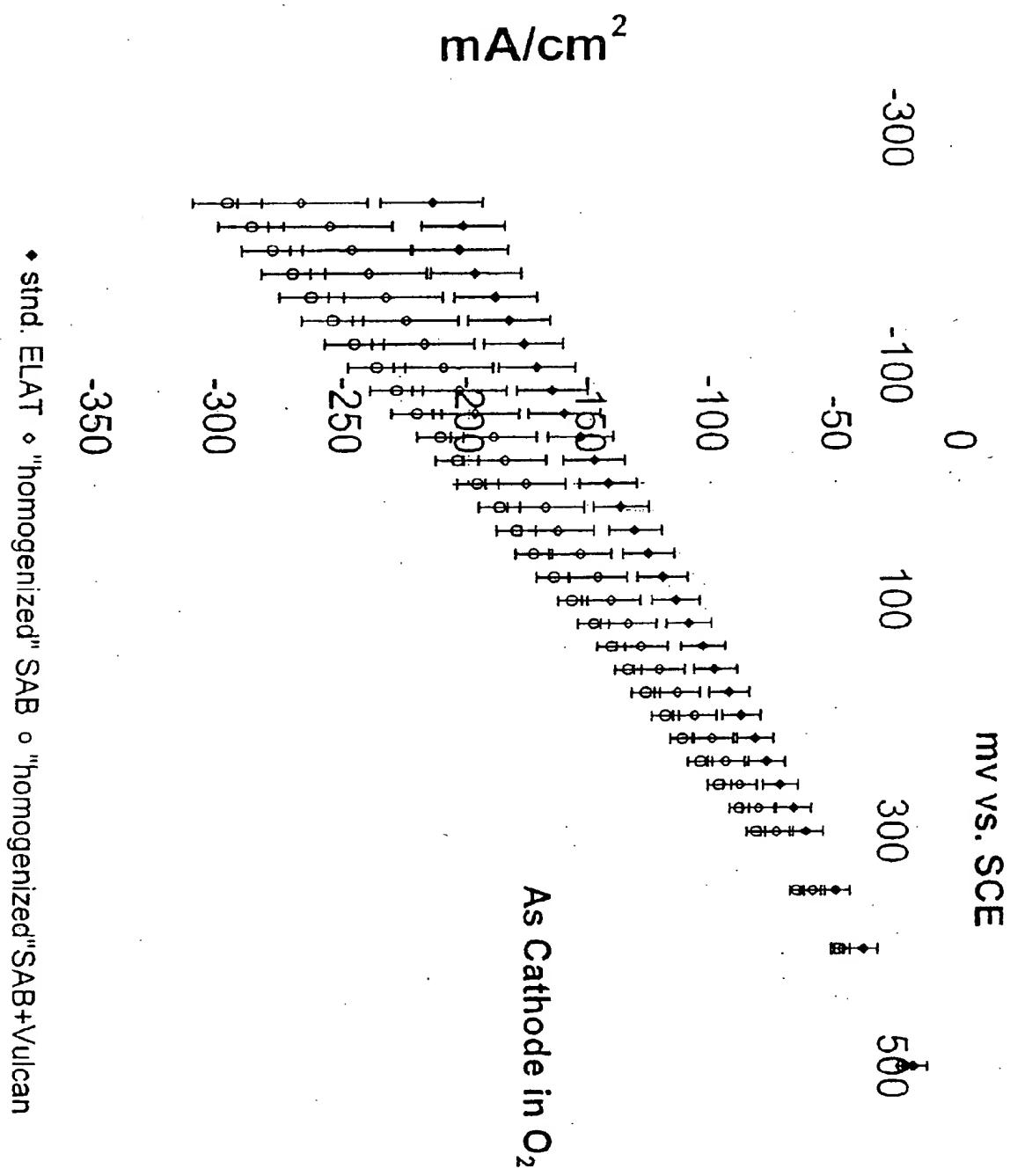
FIGURE 2

Current, mA/cm^2

mV vs. SCE

◆ stnd. ELAT
O Type "A"

FIGURE 3

mA/cm^2

mv vs. SCE

As Cathode in O$_2$

◆ stnd. ELAT ⬦ "homogenized" SAB ○ "homogenized"SAB+Vulcan

FIGURE 4

mA/cm^2

As Anode in H$_2$

mv vs. SCE

◆ stnd. ELAT ◇ "homogenized" SAB ○ "homogenized" SAB+Vulcan

FIGURE 5

Cell Voltage (volts)

Current Density (ma/cm²)

—◆— Ave.stnd. ELAT

—⊖— "Homogenized" Cathode

FIGURE 6

FIGURE 7

Cell Voltage

Current Density (A/cm²)

New
Old

FIGURE 8

FIGURE 9

Cell Voltage (V)

Current Density (ma/cm²)

◆ Hand Made Type "A"
✕ Machine Coated Type "A"

FIGURE 10

LPM/cm H$_2$O/cm^2

Type and Thickness
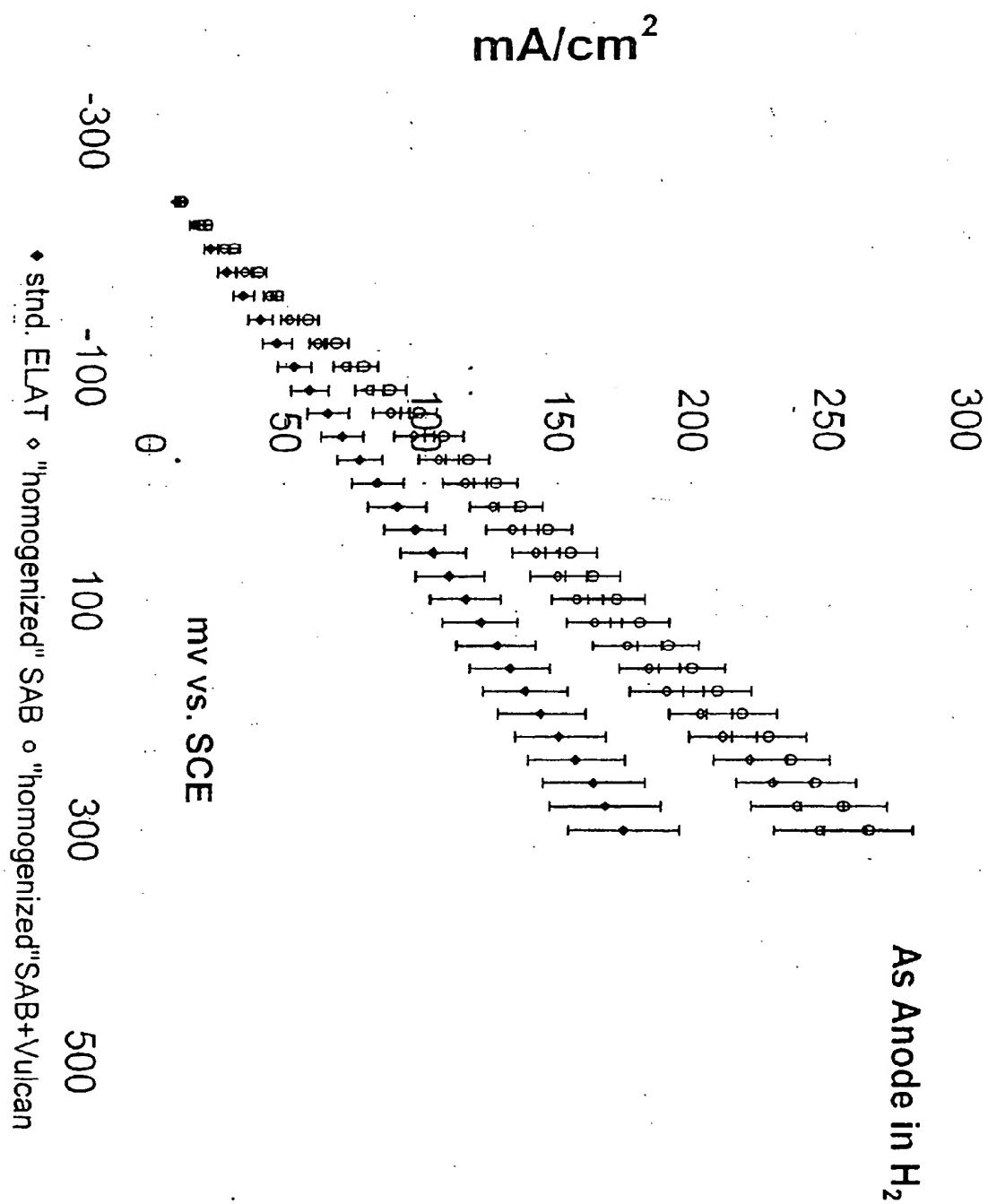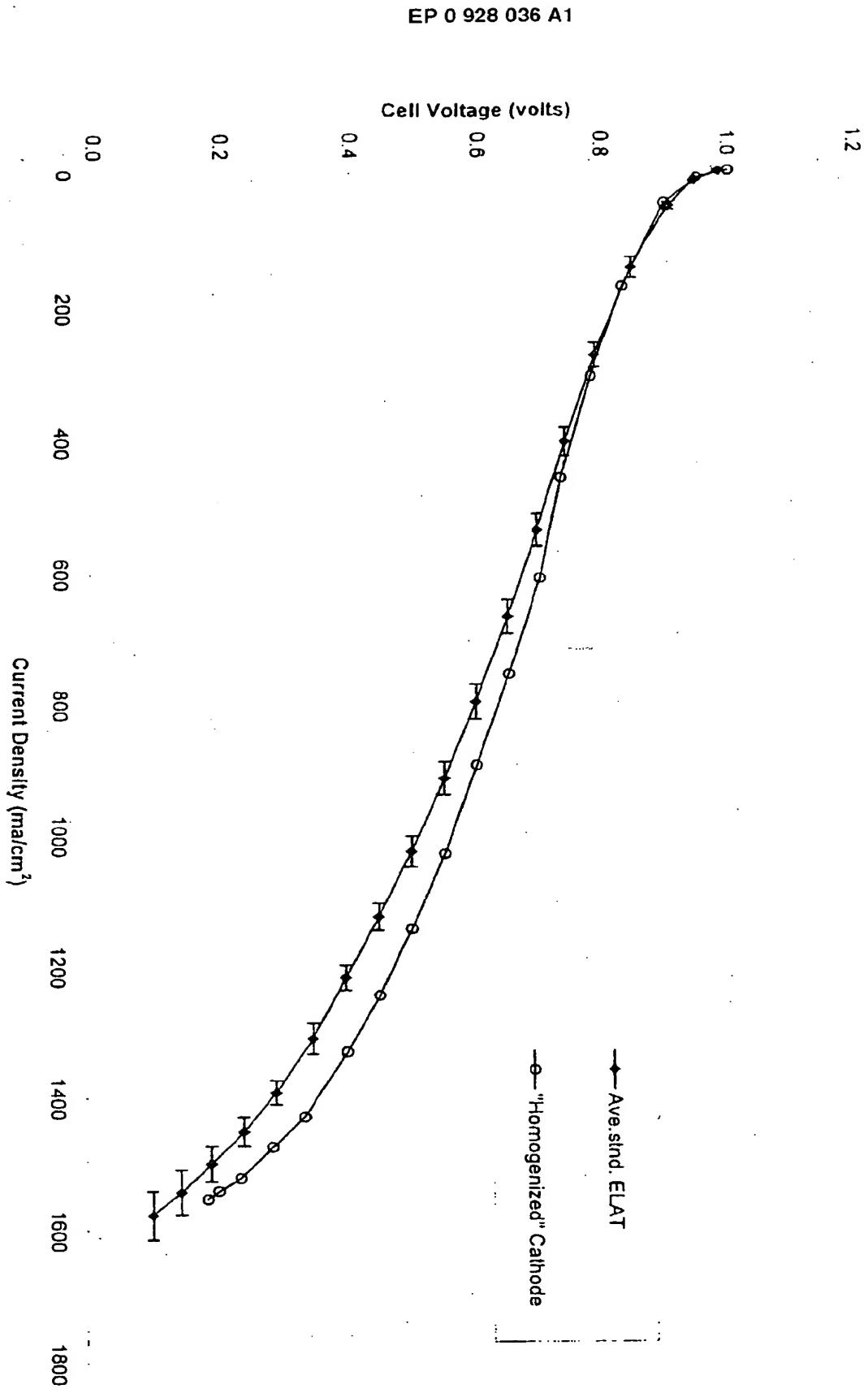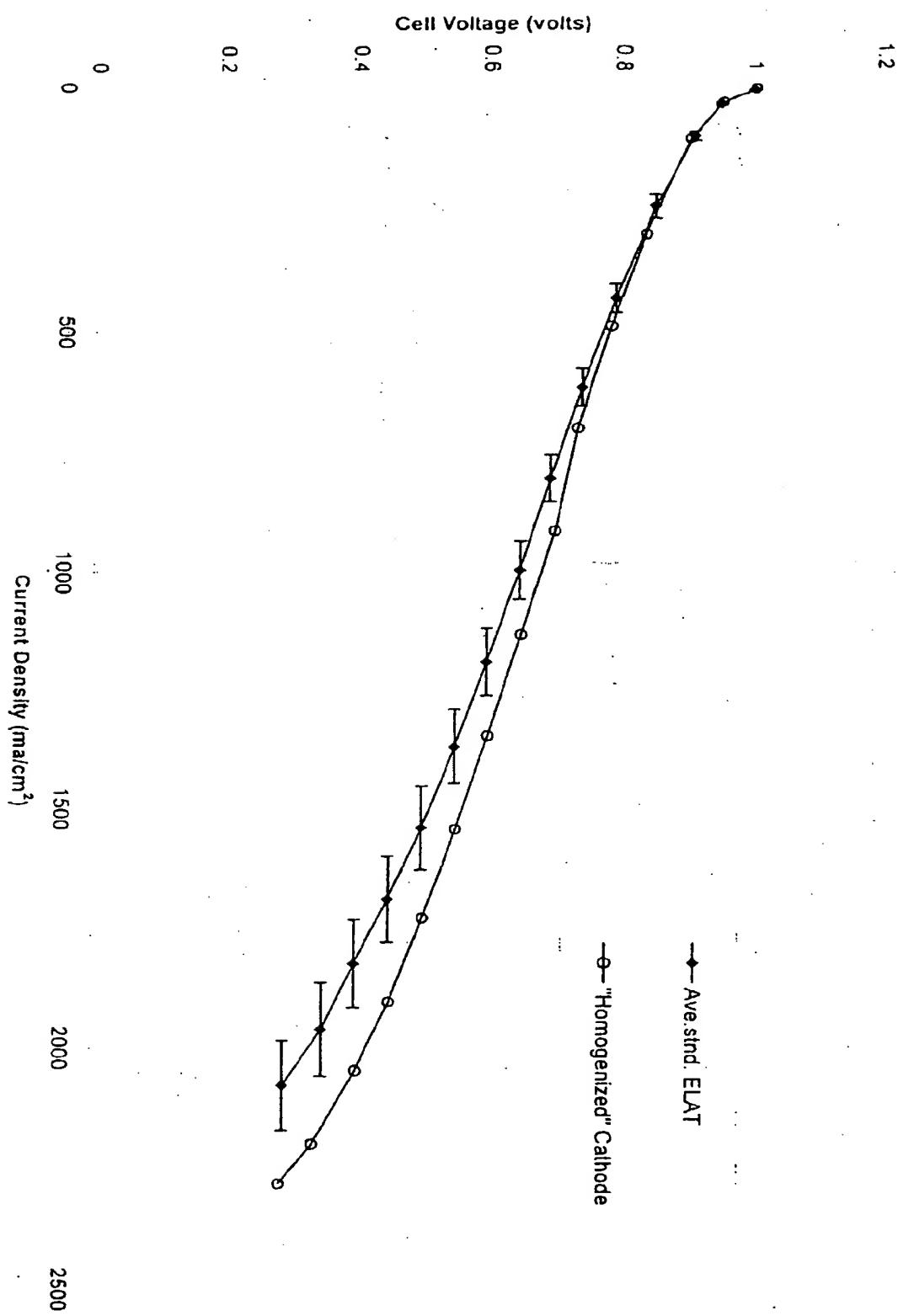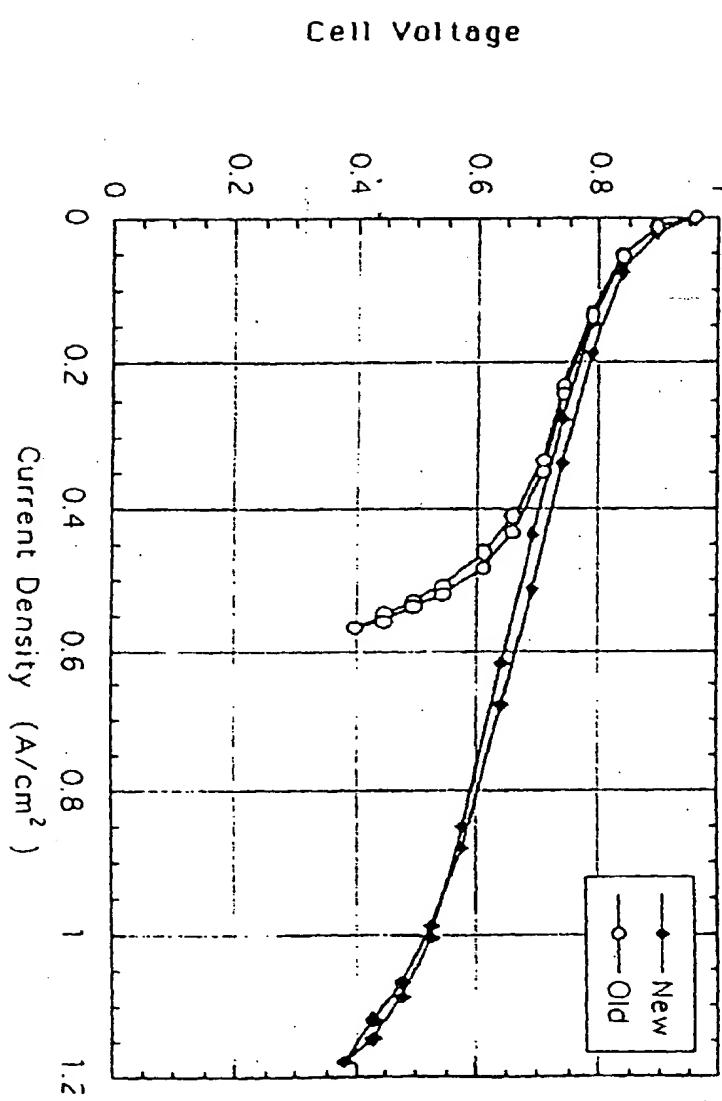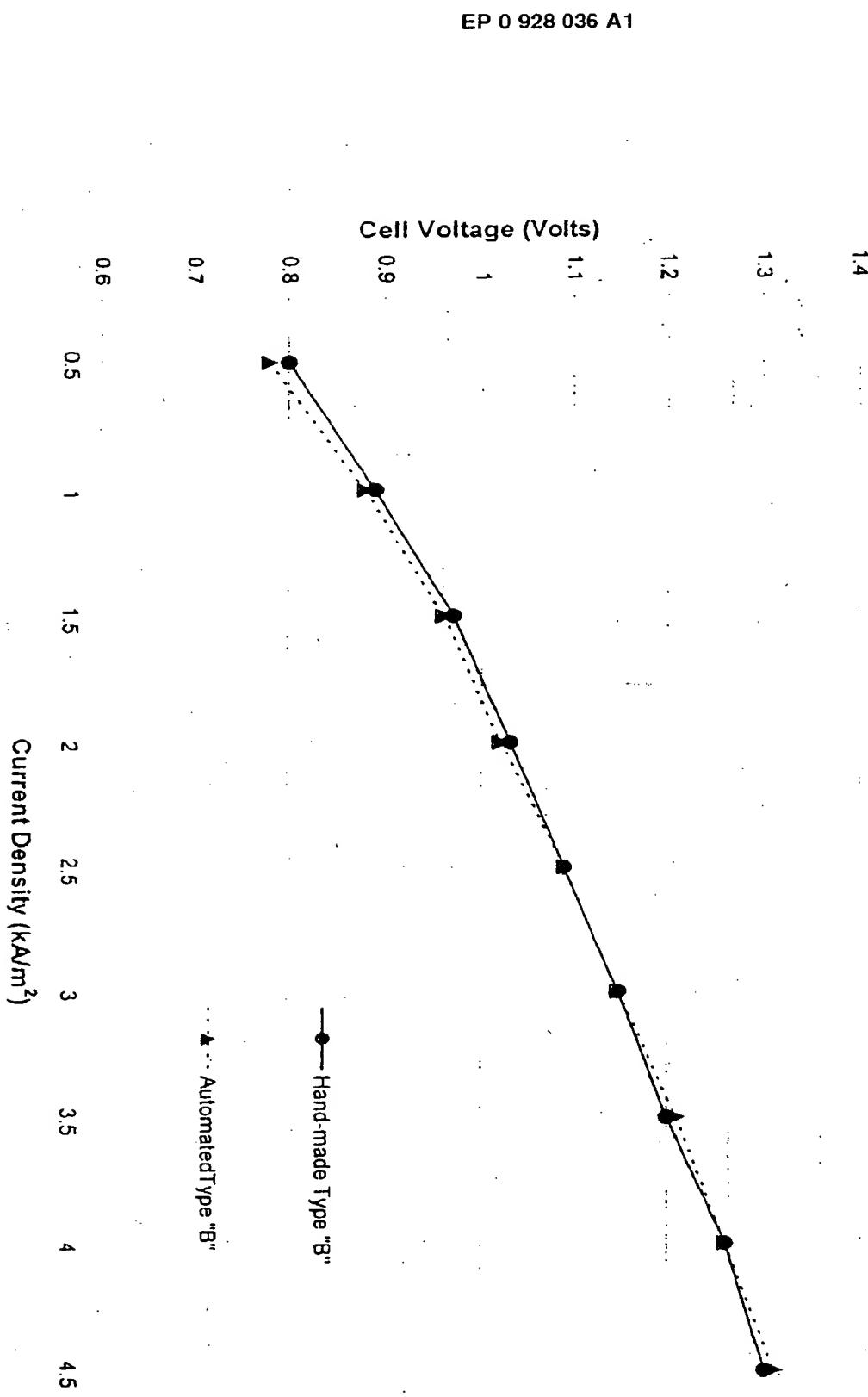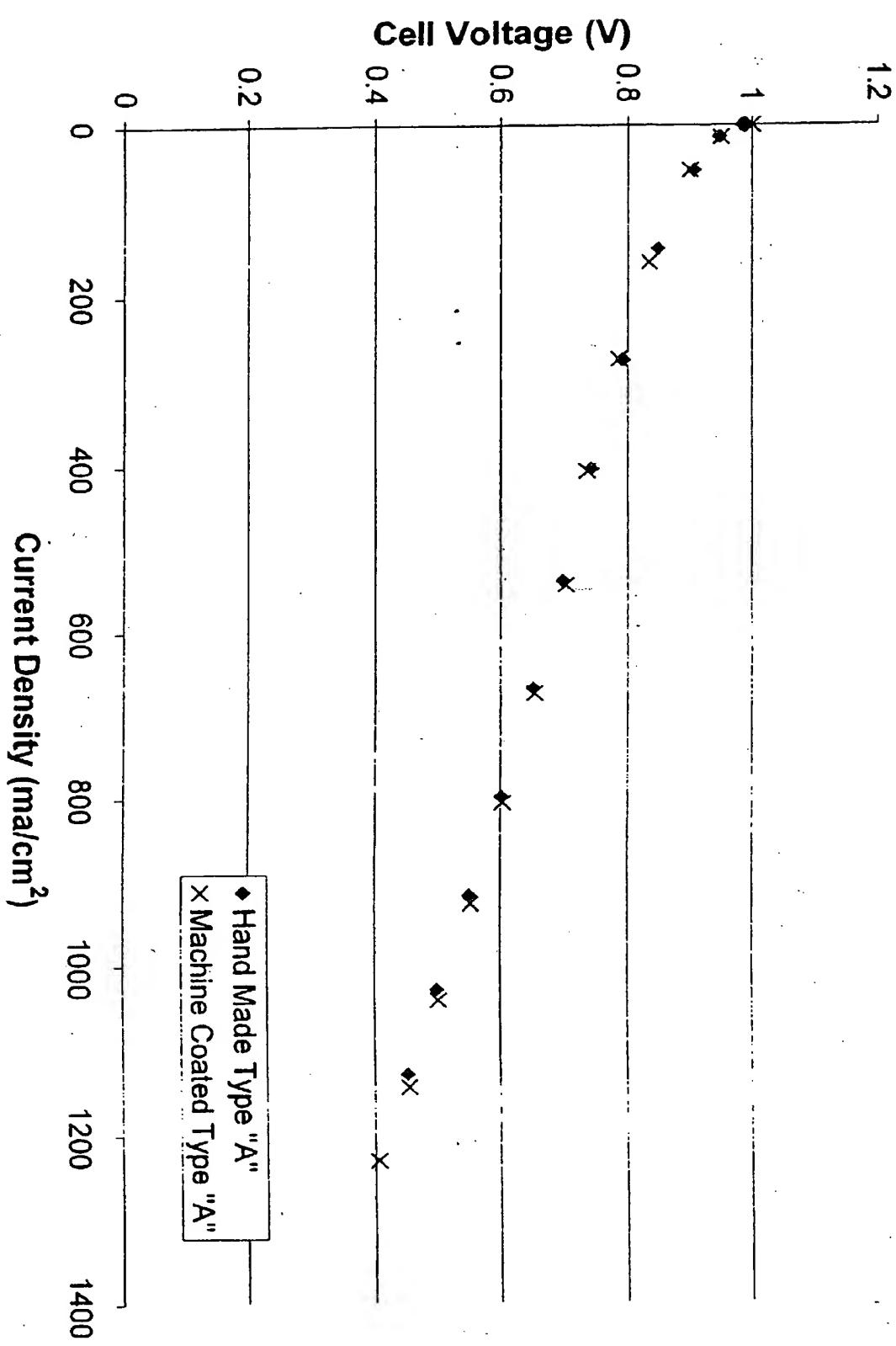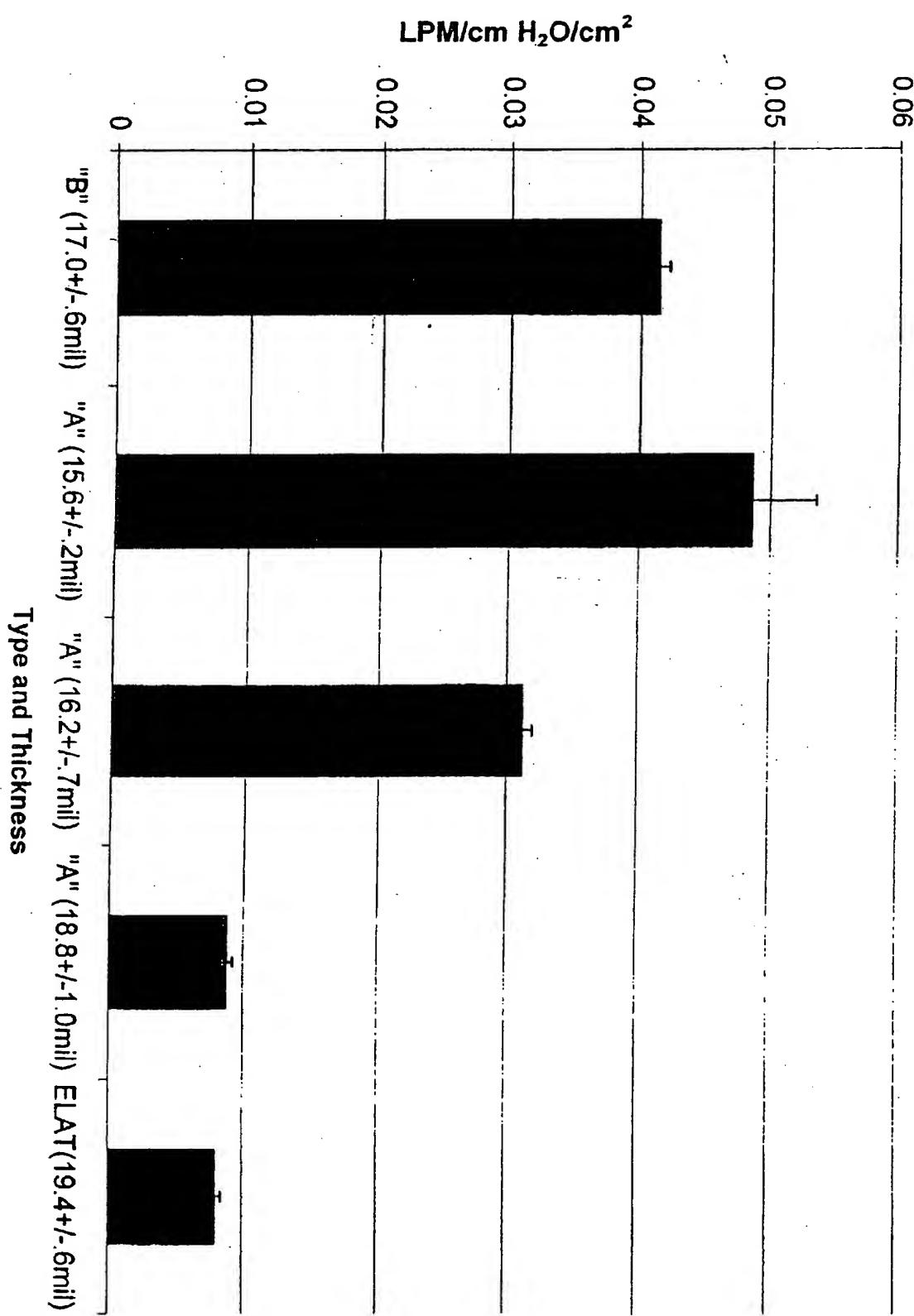
Figure 11
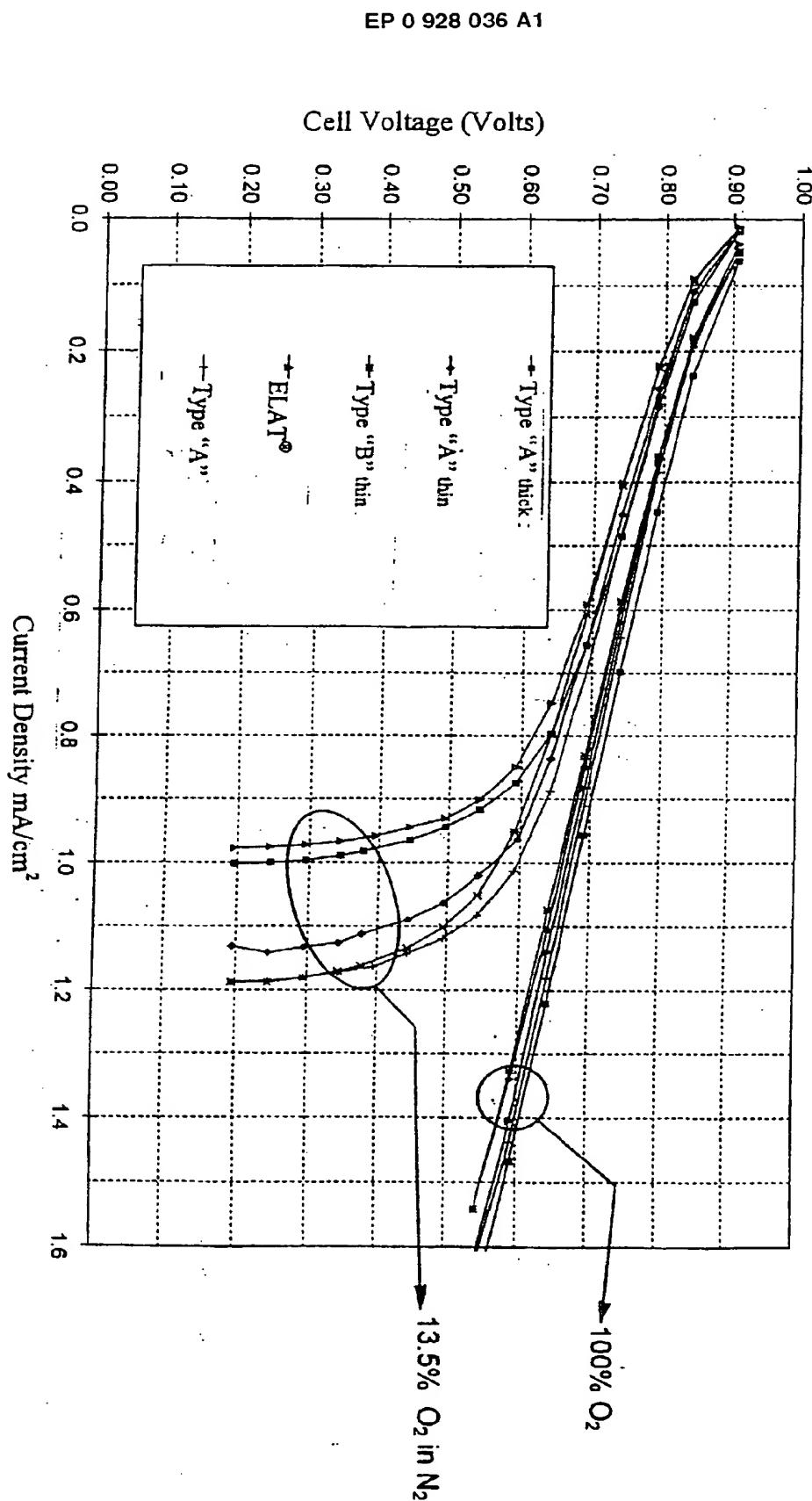
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
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O : non-written disclosure
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T : theory or principle underlying the invention
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